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Department of Chemistry

Progress Report

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STUDIES IN MOLECULAR COLLISION PHENOMENA

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Herschel Rabitz
Principal Investigator

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Molecular dynamics studies at Princeton are reviewed. The areas of research involved are:

1. molecular collisions
2. radiation-molecule interaction
3. sensitivity theory
4. finite elements in quantum mechanics.

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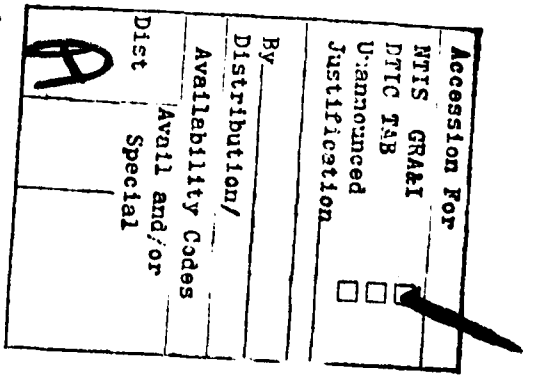
I. Contract Description

The research is concerned with molecular interactions and how they manifest themselves in a variety of physical phenomena. Emphasis is on attaining a better fundamental understanding of molecular dynamics as well as on the study of practical applications.

II. Scientific Problem

The aim of this research is to achieve a detailed understanding of the mechanism of chemical reaction dynamics and energy transfer at a molecular level. This information is of fundamental importance to molecular physics and chemistry as well as being essential for engineering design studies of many practical devices. The research is focussed on discerning the fate of excited molecules, particularly in a gaseous medium. Such excited molecules could react or transfer their excitation to other molecules upon collisional impact. In addition, an excited polyatomic molecule could undergo self-relaxation or scrambling of its internal energy even without a collision. The basic computed quantities are rate constants for these processes. An effort is under way to map out the relationship between observable laboratory behavior and the underlying input forces between the molecules. In addition to achieving a basic theoretical understanding of these processes, the research is being used to provide a framework for the analysis and inversion of appropriate measurements to yield detailed molecular rate information.



III. Scientific and Technical Approach

The varied nature of the research has necessitated a multi-faceted approach. For the treatment of polyatomic molecular dynamics an entirely new stochastic theory is being developed. This theory is designed to handle the commonly arising cases exhibiting many strongly coupled molecular levels. Both intermolecular and intramolecular situations are being treated. In addition, a vigorous effort is under way to quantum mechanically handle reactive scattering by means of finite element theory formerly developed for structural mechanics problems. Other specialized integral equation techniques are also being utilized to efficiently solve the dynamical equations. Finally, a general sensitivity theory is being pursued to provide for critical parameter analysis in macroscopic kinetics as well as in microscopic molecular processes. The sensitivty theory is based on the use of special Green's function methods, and the approach shows promise for application to a number of engineering and chemical physics problems.

IV. Research Progress

Outlined below are the specific areas of progress during the past year. The cited references are from the list of publications resulting from this contract.

1. Computational kinetics and sensitivity analysis of hydrogen-oxygen combustion.[1]

   Kinetic modelling calculations on the H_2-O_2 system were carried out with an extensive reaction set to probe the vicinity of the three explosion limits. Sensitivity analysis was used throughout this investigation to study system behavior, in particular, to

elucidate mechanistic details. The concentration and sensitivity profiles were discussed in light of appropriate experimental results and existing theories of hydrogen combustion. The results indicate the present model to be useful over a wide pressure-temperature range. The reaction set is also used to probe the sensitivities for an experimental study designed to measure rate constants of an important elementary reaction, $H + O_2 + M \rightarrow HO_2 + M$, involved in this system. The versatility of the reaction set was also demonstrated by a study of a related chemical reaction, the decomposition of hydrogen peroxide. Finally, the prospects for utilizing the methods and results of this study to examine other complex kinetic schemes were considered.

2. Chemical kinetic functional sensitivity analysis: elementary sensitivies.[2]

Sensitivity analysis was considered for kinetics problems defined in the space-time domain. This work extended earlier temporal Green's function method to nowhandle calculations of elementary functional sensitivies $\frac{\delta u_i}{\delta \alpha_j}$ where u_i is the i-th species concentration and α_j is the j-th system parameter. The system parameters can include rate constants, diffusion coefficients, initial conditions, boundary conditions, or any other well-defined variables in the kinetic equations. These parameters are generally considered to be functions of position and/or time resulting in functional derivatives $\frac{\delta u_i}{\delta \alpha_j}(x,t;x',t')$ which measure the sensitivity of species i at position x and time t with respect to a variation in the j-th parameter at position x' and prior time t'.

Derivation of the governing equations for these sensitivities and the Green's function was presented. The physical interpretation of the Green's function matrix elements was elaborated. A given element, $G_{ij}(x,t;x',t')$ can be interpreted as a generalized memory function which has important physical consequences for the design of kinetic systems. A family of reduced sensitivity coefficients was defined in terms of integrals over the functional sensitivities such that a variety of laboratory questions can be addressed. Finally, a discussion of the relation of this work to earlier research was presented.

3. The selective preparation of excited vibrational states using the stimulated resonance Raman effect.[3]

A non-perturbative treatment of stimulated resonance Raman (SRR) scattering was developed in order to study the feasibility of laboratory experiments for the selective preparation of highly excited vibrational molecules. The theory is based on the derivation of an effective Hamiltonian for the interaction of the electric field with molecular electronic-vibrational-rotational states. The resulting reduction in the number of coupled differential equations describing the SRR effect allowed for a convenient numerical solution, which is important in intense laser fields. In addition, when the spectral transitions are power-broadened to a considerable extent, the solutions become analytic. An application of the theory to the I_2 system shows the possibility of selectively populating high vibrational levels ($v' \geq 10$) in the ground electronic state. A similar analysis on the O_2 system

shows favorable laboratory conditions for pumping states $v' = 4\text{-}12$. Most importantly, it now appears possible to selectively populate wide choices of vibrational levels by suitable variations in the frequencies and proper selection of the intensities and durations of the applied laser fields. Active design of laboratory apparatus is underway in conjunction with this study.

4. Further developments and applications of sensitivity analysis to collisional energy transfer.[4]

This work considered the sensitivity of integrated collision cross sections to the variations of the intermolecular potential parameters. The study was concerned with the scattering of an atom with a linear rigid rotor and an atom with a breathing sphere. Attention was focused upon first order sensitivity coefficients (i.e., the gradient of the cross sections with respect to potential parameters), from which an entire family of derived sensitivity coefficients may be obtained. The original elementary set of sensitivities are expressed as $\frac{\partial \sigma_{j \to j'}}{\partial \sigma_i}$ where α_i is the i-th system parameter. Within the family of derived sensitivities a special class of coefficients $\frac{\partial \alpha_r}{\partial \alpha_p}$ was shown to be particularly important in determining the extent to which a set of measurements is able to define the parameters of an assumed potential. In addition, the derived sensitivities $\frac{\partial \sigma_{j \to j'}}{\partial \sigma_{\ell \to \ell'}}$ have an immediate bearing on the interdependence for different possible laboratory measurements. Finally, the global behavior of cross sections in parameter space was examined and a non-linear interpolation formula was derived utilizing sensitivity information. The utility of this latter formula is illustrated in Figure 1.

5. Sensitivity analysis of rotational energy transfer processes to the intermolecular potential.[5]

This research considered the sensitivity of rotational energy transfer processes to variations of parameters within an assumed model intermolecular potential. The following cross sections were examined: integral state-to-state, pressure broadening, effective diffusion and viscosity, and final state summed integral cross sections. In order to simplify the calculation of cross sections, attention was restricted to the scattering of an atom and a linear rigid rotor. Furthermore, the collision dynamics are approximated by using the infinite order sudden (IOS) method. Particular attention was focused upon the sensitivities of different cross sections and combinations of cross sections to the various parameters. The first order sensitivities were also used to derive new coefficients which describe how the potential parameters correlate given a limited set of cross section data. These coefficients are shown to be especially important in determining the degree to which a set of measurements is able to define various parameters of an assumed potential.

6. Sensitivity analysis of differential cross sections to the intermolecular potential.[6]

This research treated the sensitivity of both final state summed and state-to-state differential cross sections to variations of parameters within a model intermolecular potential. In order to simplify the calculations of the cross sections and first order sensitivty coefficients (i.e., the partial derivative of the cross

sections with respect to potential parameters (attention was restricted to the scattering of an atom and a rigid rotor. Figure 2 gives an example of a particular cross section and its associated sensitivity derivatives. Special emphasis was given to an examination of the sensitivity of angular features of the cross sections to potential parameter variations. This is facilitated by fitting the cross sections to functional forms which contain several adjustable parameters, each of which controls a particular feature. The first order sensitivity coefficients were then used to derive quantities which measure the sensitivity of a feature parameter with respect to variations of a potential parameter. The first order sensitivities were also used to obtain so-called derived sensitivity coefficients; this particularly involved those which describe how the potential parameters are interrelated for a given set of differential cross section measurements. The behavior of these coefficients was examined as the angular range of the measurements was varied and as account was taken of the finite angular resolving power of molecular beam detectors. The results were used to determine the degree to which a set of differential cross section measurements is able to define various parameters of an assumed potential.

7. Action angle variables for the quantum three particle system.[7]

This work used the newly developed quantum action angle variable formalism to reduce the three-atom interaction system to a minimum of four independent coordinates. A transformation was also presented which converted the Hamiltonian to a form amenable to

the direct numerical integration of the resultant Schrödinger equation. Computational considerations relevant to the application of finite elements were also discussed and illustrated with a numerical calculations of the quantum energy levels of a rigid asymmetric rotor. The ordinary differential equation derived for this last problem permits an unambiguous assignment of the quantum expression for the total angular momentum.

8. The collision of two linear rotors: a scaling theoretical analysis of the H_2-H_2 and HF-HF systems.[8]

An energy corrected sudden scaling theory was applied to rotation-translation and rotation-rotation energy transfer in the H_2-H_2 and HF-HF systems. The scaling predictions are in very good agreement with the exact quantal values. Two physically important results are particularly transparent in the scaling analysis: (1) The well-known effectiveness of ortho-H_2 in rotational relaxation can be traced directly to the higher tensor order interactions which are also operative in para-H_2 for $j \geqslant 0$; and (2) transitions in which rotational quanta are conserved differ appreciably from those in which rotational quanta are not conserved. Scaling predictions using different values for the average collision range ℓ_c, were compared to the exact quantal cross sections. The results indicated that essentially the same value of ℓ_c will be determined by inspection of the dynamical solutions and by the scaling analysis. This point is of importance for future applications of the scaling theory to the inversion of laboratory data.

9. A comparison between finite element methods and spectral methods as applied to bound state problems.[9]

The finite element and spectral methods were applied to two-dimensional bound state problems. A comparison of the spectral method, which requires a global basis set expansion of the wave-functions, and the finite element method, which requires no such expansion, was performed. A procedure was given for formulating the finite element approach and for achieving fast and accurate results. The convergence of the finite element calculations was considered and shown to be well behaved. The basic conclusion of this work is that the finite element and spectral methods are complementary. In the regime where an accurate zero-th order Hamiltonian can be identified the spectral method excels. On the other hand, finite element theory is better for complex potentials that do not lend themselves to conventional eigenfunction expansions. A discussion of the extension of the finite element method to higher dimensions was also included in this work.

10. An improved phase shift approach to the energy correction of the infinite order sudden approximation.[10]

A new method was developed for obtaining energy corrections to the infinite order sudden (IOS) approximation by incorporating the effect of the internal molecular Hamiltonian into the IOS wave function. This was done by utilizing the JWKB approximation to transform the Schrödinger equation into a differential equation for the phase. It was found that the internal Hamiltonian generates an effective potential from which a new improved phase shift is obtained. This

phase shift is then used in place of the IOS phase shift to generate new transition probabilities. As an illustration the resulting improved phase shift (IPS) method was applied to the Secrest-Johnson model for the collinear collision of an atom and diamtom. In the vicinity of the sudden limit, the IPS method gives results for transition probabilities, $P_{n\to n+\Delta n}$, in significantly better agreement with the 'exact' close coupling calculations than the IOS method, particularly for large Δn.

11. Stochastic theory of intermolecular energy transfer in in the presence of radiation.[11]

A theory for internal energy redistribution in polyatomic molecules perturbed by strong radiation fields was constructed. Use was made of stochastic theory, which assumes a random phase approximation is valid after appropriate time intervals. This approximation permits the Schrödinger equation to be replaced with a finite-difference master equation for the probabilities of occuyping the various quantum levels. The semiclassical theory of the radiation-molecule interaction was employed in this work. The laser linewidth and rotational effects are incorporated into the formalism. At each stochastic step the energy changes in the molecules due to radiation are estimated. Thus energy conservation is explicitly taken into account. Model calculations for SO_2, whose transition dipole moment matrix elements and anharmonic force constants have been determined, indicate a complex interplay of anharmonic and radiative coupling. Power density, laser linewidth and detuning from resonance are observed to play a significant role in energy redistribution.

Publications Resulting from Research Under this Contract.

1. E. Dougherty and H. Rabitz, " Computational Kinetics and Sensitivity Analysis of Hydrogen-Oxygen Combustion", J. Chem. Phys. 72, 6571 (1980).

2. M. Demiralp and H. Rabitz, " Chemical Kinetic Functional Sensitivity Analysis: Elementary Sensitivities", J. Chem. Phys., in press.

3. A. DePristo, H. Rabitz and R. Miles, " The Selective Preparation of Excited Vibrational States Using the Stimulated Resonance Raman Effect", J. Chem. Phys., in press.

4. L. Eslava, L. Eno and H. Rabitz, " Further Developments and Applications of Sensitivity Analysis to Collisional Energy Transfer", J. Chem. Phys., in press.

5. L. Eno and H. Rabitz, " Sensitivity Analysis of Rotational Energy Transfer Processes to the Intermolecular Potential", J. Chem. Phys. 72, 2314 (1980).

6. L. Eno and H. Rabitz, " Sensitivity Analysis of Differential Cross Sections to the Intermolecular Potential", J. Chem. Phys., submitted.

7. S. Augustin, M. Demiralp, H. Rabitz and A. Askar, " Action-Angle Variables for the Quantum Three Particle System", J. Chem.Phys. 73, 268 (1980).

8. A. DePristo and H. Rabitz, " The Collision of Two Linear Rotors: A Scaling Theoretical Analysis of the H_2-H_2 and HF-HF Systems" , J. Chem. Phys. 72, 4685 (1980).

9. M. Duff, H. Rabitz, A. Askar, A. Cakmak and M. Ablowitz, " A Comparison Between Finite Element and Spectral Methods as Applied to Bound State Problems", J. Chem. Phys. 72, 1543 (1980).

10. B. Chang, L. Eno and H. Rabitz, " An Improved Phase Shift Approach to the Energy Correction of the Infinite Order Sudden Approximation", J. Chem. Phys. 73, 820 (1980).

11. E. Dougherty, S. Augustin and H. Rabitz, " Stochastic Theory of Intramolecular Energy Transfer in the Presence of Radiation", J. Chem. Phys., in press.

Figure Captions

Figure 1. An illustration of collisional parameter scaling for two breathing sphere cross sections. The parameter δ controls the vibrational coupling in the system. The solid curve is obtained by laboriously repeating the calculations at new δ values, while the dashed curve is a result of using the sensitivity analysis generated scaling theory. Excellent results are obtained, particularly in comparison to using perturbation theory indicated by the dash-dot line.

Figure 2. The top panel shows the $0 \rightarrow 4$ differential cross section and the panels below it are sensitivity coefficients with respect to the overall potential strenth $\bar{\epsilon}$, the well depth anisotropy a, the range parameter $\bar{R}_m$ and finally the range anisotropy b. The minimum in the cross section near 80^o is due to rotational motion interference and the striking structure in the sensitivities at this angle can be readily used to interpret the physical origin of this structure.

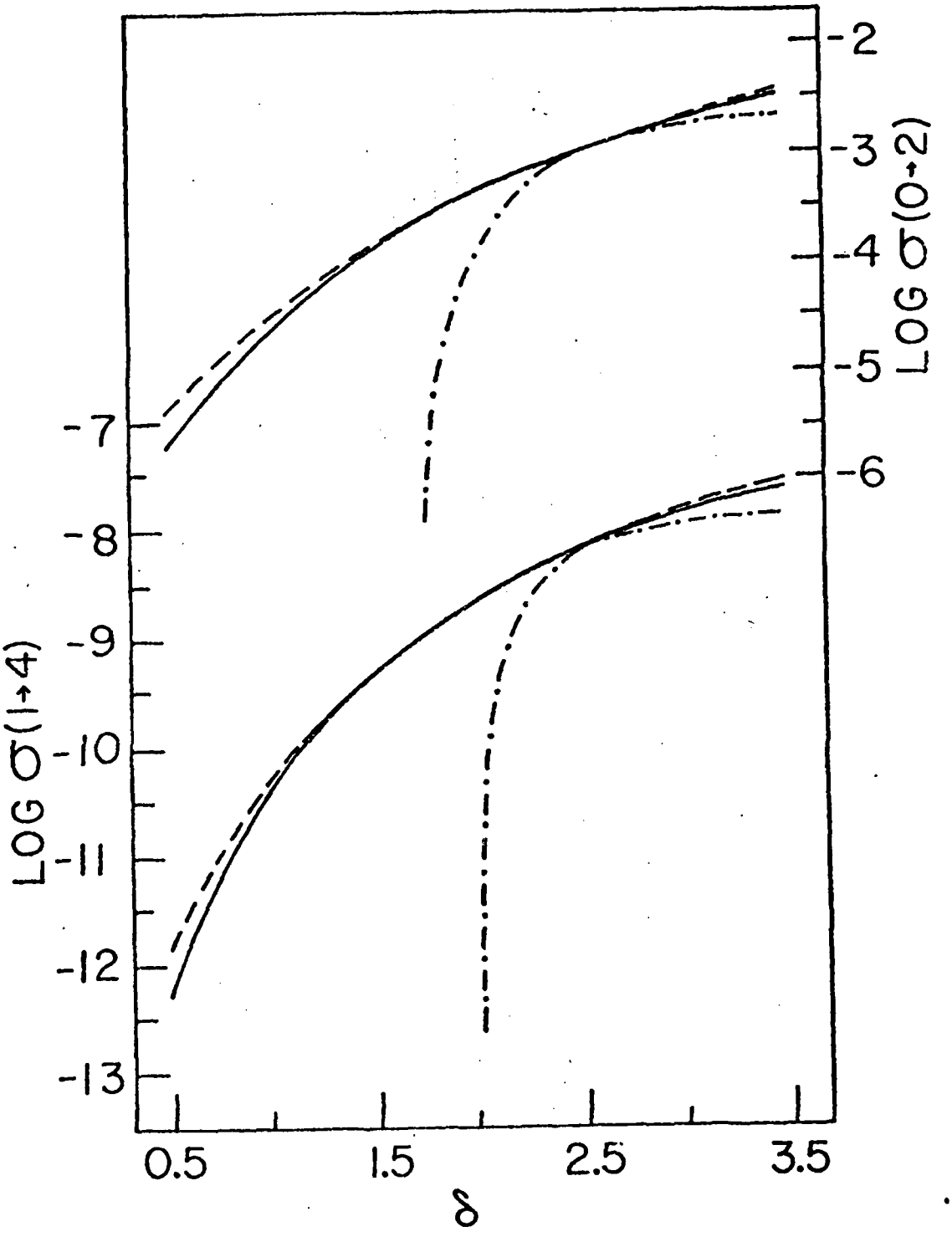


Figure 1

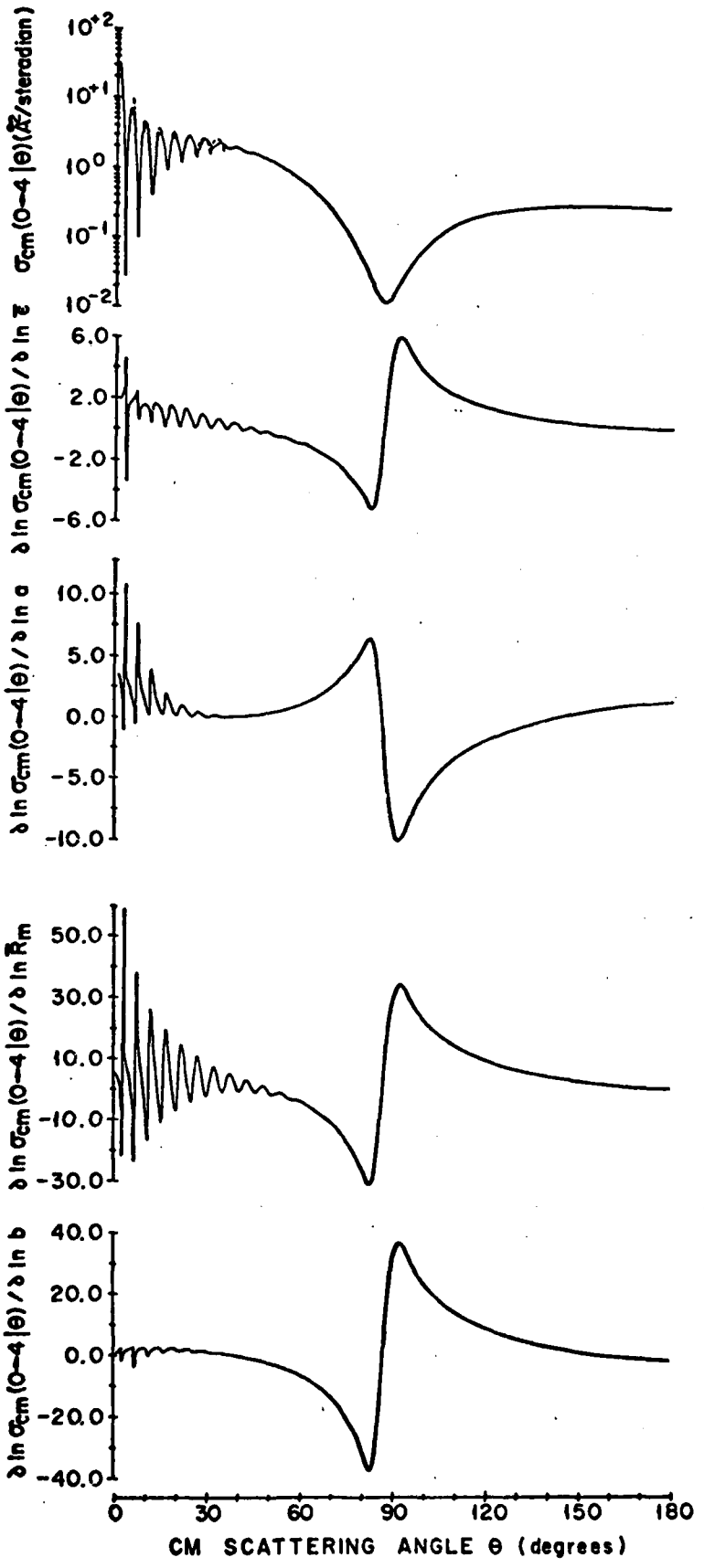

$\sigma_{cm}(0-4|\theta)$(Å²/steradian)
10^{+2}
10^{+1}
10^{0}
10^{-1}
10^{-2}
$\partial \ln \sigma_{cm}(0-4|\theta) / \partial \ln \varepsilon$
6.0
2.0
-2.0
-6.0
$\partial \ln \sigma_{cm}(0-4|\theta) / \partial \ln a$
10.0
5.0
0.0
-5.0
-10.0
$\partial \ln \sigma_{cm}(0-4|\theta) / \partial \ln R_m$
50.0
30.0
10.0
-10.0
-30.0
$\partial \ln \sigma_{cm}(0-4|\theta) / \partial \ln b$
40.0
20.0
0.0
-20.0
-40.0
0
30
60
90
120
150
180
CM SCATTERING ANGLE θ (degrees)

Figure 2

VI. Personnel

Stuart Augustin
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Postdoctoral Associate

Larry Eno
Postdoctoral Associate

Britton Change
Graduate Student

Eugene Dougherty
Graduate Student (Ph. D., 1980).

Luis Eslava
Graduate Student